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## EUROPEAN PATENT APPLICATION

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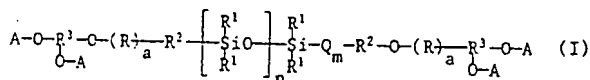
71 Applicant: CIBA-GEIGY AG  
Klybeckstrasse 141  
CH-4002 Basel (CH)

72 Inventor: Mueller, Karl F.  
119 West 77th Street  
New York New York 10024 (US)

Harisiades, Paul  
150 Pinecrest Drive  
Hastings-on-Hudson New York 10706-3702 (US)

54 Terminal polyvinyl functional macromers, polymers thereof and contact lenses made therefrom.

57 Disclosed is a poly-unsaturated polysiloxane of the formula



wherein at least three of A are a reactive vinyl containing group as defined in the specification and the further variables are as defined in the specification. The invention concerns even polymers of those compounds and copolymers thereof with up to 95 % of one or more hydrophilic or hydrophobic reactive vinyl monomers, or mixture thereof. The respective (co)polymers are suitable for the manufacture of contact lenses.

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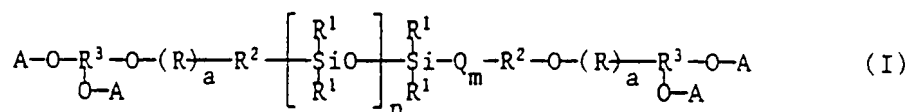
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(71) Applicant: **CIBA-GEIGY AG**  
**Klybeckstrasse 141**  
**CH-4002 Basel(CH)**

(72) Inventor: **Mueller, Karl F.**  
**119 West 77th Street**  
**New York New York 10024(US)**  
Inventor: **Harisiades, Paul**  
**150 Pinecrest Drive**  
**Hastings-on-Hudson New York**  
**10706-3702(US)**

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**EP 0 291 452 A3**



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-4 640 940 (A.F. JACOBINE) * Claims 1,3,4,5; column 5, lines 13-68; example 9; columns 8,9 *	1-10	C 08 G 77/38 G 02 B 1/04 C 08 F 299/08 C 08 F 230/08
D,X	US-A-4 486 577 (K.F. MUELLER) * Claims 1-28; column 5, lines 34,35; column 6, lines 1-3; column 11, lines 44-46; column 12, lines 5-27,52-68; column 13, lines 1-22 *	1-24	
X	EP-A-0 176 481 (CIBA-GEIGY) * Claims 1-38 *	1-24	
A	DE-A-3 006 167 (SHIN-ETSU) * Claim 1 *	1	
A	EP-A-0 018 624 (Th. GOLDSCHMIDT) * Claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 F C 08 G G 02 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-10-1990	Examiner DEPIJPER R.D.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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## Description

## Terminal polyvinyl functional macromers, polymers thereof and contact lenses made therefrom

Unsaturated low molecular weight polymers are widely used in the resins industry, for example as UV-curable coatings and paints, or in the fabrication of molded parts. Typical examples of such unsaturated polymers are the di(meth)-acrylates obtained by reaction of a polyether or a polyester diol with, first, 2 equivalents of a diisocyanate, followed by termination with an hydroxyalkyl (meth)-acrylate, as. e.g. described in US patent 3,509,234 and 4,192,827.

Polysiloxane analogs of such divinyl polymers are described in US patent 4,136,250 and 4,486,577. Direct esterification of polymeric diols with acryl or methacryl dichloride can also be used to make these polymeric di(meth)acrylates, which have found wide use in UV-curable coatings and also, with polysiloxanes as main components, in the contact lens area, because of their high oxygen permeability.

An alternate method for making these divinyl polymers is by reaction of the diol or diamine prepolymer with an unsaturated isocyanate, most commonly isocyanatoethylmethacrylate (IEM). This method has the advantage that no chain extensions can occur and no volatile components or water have to be removed. Unsaturated polymers based on this reaction have been described in US patent 4,338,242 and 4,529,765. Unsaturated polysiloxanes made by this method are described in US patent 4,563,539 and 4,605,712.

All these divinyl polymers give on polymerization crosslinked polymers, just like low molecular weight (MW) divinyl compounds; in the coatings industry, high MW divinyl compounds are often used alone, without the addition of highly toxic, volatile comonomers, or they are used in combination with low MW di- or tri- or tetra(meth)acrylates in order to increase crosslinked density. Often such mixtures are incompatible because of differences in solubility parameters and because the relatively high MW divinyl-polymers (MW, typically range from 1000-10000) are poorly miscible with other polymeric components.

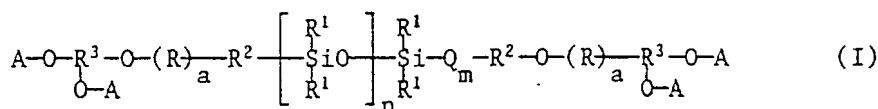
When polysiloxane-di or tri(meth)acrylates are used to make gas permeable contact lens materials, additional crosslinking agents, like ethylene glycol dimethacrylate, have often to be added to achieve sufficient rigidity. Even then, the additional hydrogen bonding chain interaction derived from multiple urethane linkages are necessary for making a high modulus polymer.

A high urethane content of the divinyl-polysiloxane prepolymer has also been found to help compatibility with many comonomers especially acrylic monomers, which are commonly used in the fabrication of contact lens materials, and in which high optical clarity is of greatest importance (US patent 4,486,577).

It has now been discovered that polysiloxane prepolymers terminated with at least three vinyl groups give polymers with superior hardness and oxygen permeability.

These polyvinyl-polysiloxanes are superior to the di- or tri-vinyl polysiloxanes of prior art in most applications where product stiffness and compatibility with comonomers is important.

One embodiment of the present invention relates to a poly-unsaturated polysiloxane of the formula I,

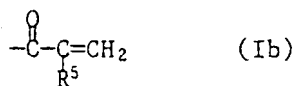
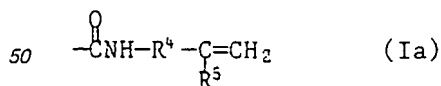


wherein a is zero or one;

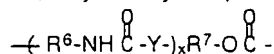
n is 2 to about 500;

m is zero to 2;

at least three of A either consist of a reactive vinyl containing group of the formula Ia or Ib, and the remaining A are hydrogen or said reactive vinyl containing group Ia or Ib,



where R<sup>4</sup> is arylene of 6 to 12 carbon atoms, alkarylene of 7 to 14 carbon atoms, alkylene of up to 8 carbon atoms, alkyleneoxy of up to 8 carbon atoms or a group of the formula



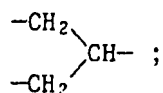
where R<sup>7</sup> is alkylene of 2 to 8 carbon atoms, x is zero or one, Y is -O- or -NR<sup>8</sup>- where R<sup>8</sup> is hydrogen or alkyl of up to 4 carbon atoms, and R<sup>6</sup> is the diradical residue of an aliphatic, cycloaliphatic, aromatic or araliphatic diisocyanate;

and R<sup>5</sup> is hydrogen or methyl;

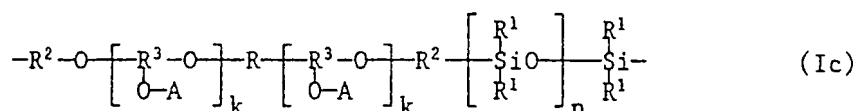
R<sup>1</sup> is alkyl of up to 4 carbon atoms or phenyl;

R<sup>2</sup> is alkylene of 2 to 6 carbon atoms;

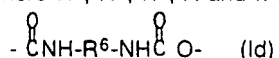
$R^3$  is  $-\text{CH}_2-\text{CH}-\text{CH}_2-$  or



such that  $-\text{R}^3(\text{OA})_2$  is  $\text{AOCH}_2\text{CH}(\text{OA})\text{CH}_2-$  or  $(\text{AOCH}_2)_2\text{CH}-$ ;  
Q is a group of the formula Ic,



where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , A and n are as defined above; and k is zero or one; and R is a group of the formula Id



where  $\text{R}^6$  is as defined above.

Arylene of 6 to 12 carbon atoms is preferably phenylene, unsubstituted or substituted by one or more lower alkyl groups, such as e.g. methyl groups, e.g. phenylene or methyl-phenylene.

Alkarylene of 7 to 14 carbon atoms is preferably phenylene lower alkylene, wherein phenyl is unsubstituted or substituted by one or more lower alkyl groups, such as e.g. methyl groups, e.g. phenylene methylene or dimethylphenylene-methylene.

Alkylene of up to 8 carbon atoms is e.g. methylene, 1,2-ethylene, 1,3-proylene, 1,2-propylene, butylene, pentylene, or octylene.

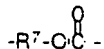
Alkyleneoxy of up to 8 carbon atoms is preferably ethyleneoxy, propyleneoxy or butyleneoxy, the oxygen atom thereof being bound to the carbon atom to which  $\text{R}^4$  is connected.

Lower alkyl preferably has up to 8 carbon atoms, more preferably up to 4 carbon atoms, and is e.g. methyl, ethyl, propyl or tert. butyl.

The diradical residue of an aliphatic, cycloaliphatic, aromatic or araliphatic diisocyanate is defined as a corresponding diisocyanate without its both  $-\text{NCO}$  groups. Thus an aliphatic diradical residue is e.g. alkylene of up to 8 carbon atoms, such as 1,6-hexylene; an aromatic diradical residue is e.g. phenylene, unsubstituted or substituted by one or more lower alkyl groups, such as methyl, e.g. methylphenylene; a cycloaliphatic diradical residue is e.g. cycloalkylene having 5 or 6 carbon atoms or cycloalkylene lower alkylene having 5 or 6 carbon atoms in the cycloalkylene moiety, both of which unsubstituted or substituted by one or more lower alkyl groups, such as methyl groups, e.g. trimethylcyclohexylene or trimethylcyclohexylene methylene; and an araliphatic diradical residue is e.g. phenylene-lower alkylene or phenylene-lower alkylene-phenylene, e.g. phenylenemethylene or phenylene-methylene-phenylene.

$\text{R}^1$  is preferably methyl.

In one preferred embodiment of the present invention, a, x and m are zero. In this embodiment, A is preferably of the formula Ia,  $\text{R}^4$  is preferably of the formula



wherein  $\text{R}^7$  is alkylene of 2 to 6 carbon atoms,  $\text{R}^2$  is alkylene of 2 to 4 carbon atoms and each  $-\text{R}^3(\text{OA})_2$  is of the formula  $\text{AOCH}_2\text{CH}(\text{OA})\text{CH}_2-$ . Most preferably,  $\text{R}^2$  is ethylene, each A is of the formula Ia and  $\text{R}^5$  is methyl.

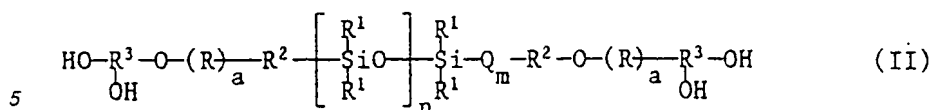
In an alternate preferred embodiment, A is of the formula Ib, a is one, m is zero,  $\text{R}^3(\text{OA})_2$  is of the formula  $(\text{AOCH}_2)_2\text{CH}-$  and  $\text{R}^5$  is methyl.

In another alternate preferred embodiment, m is 1 or 2, k is one, a is zero, A is of the formula Ia, x is zero,  $-\text{R}^3(\text{OA})_2$  is of the formula  $\text{AOCH}_2\text{CH}(\text{OA})\text{CH}_2-$  and  $\text{R}^5$  is methyl. Most preferably in this embodiment,  $\text{R}^2$  is ethylene and  $\text{R}^6$  is a divalent hydrocarbyl aliphatic, cycloaliphatic, aromatic or araliphatic group of up to 16 carbon atoms.

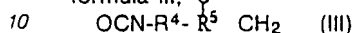
In a yet further alternate embodiment, A is of the formula Ib, a is one, m is 1 or 2, k is zero,  $-\text{R}^3(\text{OA})_2$  is of the formula  $(\text{AOCH}_2)_2\text{CH}-$  and  $\text{R}^5$  is methyl. Most preferably in this embodiment,  $\text{R}^2$  is ethylene and  $\text{R}^6$  is a divalent hydrocarbyl aliphatic, cycloaliphatic, aromatic or araliphatic group of up to 16 carbon atoms.

The poly-unsaturated polysiloxanes of formula I can be prepared by methods known in the art.

For example, compound of formula I can be prepared by reacting a polysiloxane polyol of the formula II,



wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, a, n and m are as defined above, with an isocyanato substituted vinyl compound of the formula III,  $\text{C}=\text{CH}_2$

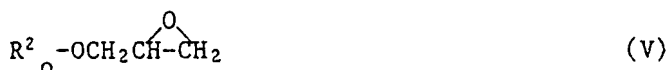


where R<sup>4</sup> and R<sup>5</sup> are as defined above, preferably in the presence of a urethane catalyst such as stannous octoate or dibutyltin dilaurate, in the presence or absence of a solvent at a temperature between ambient and 80°C. For the manufacture of compounds of formula I wherein A is of the formula Ib, a compound of formula III is replaced by the respective acrylic or methacrylic acid derivative introducing the group of formula Ib.

The compounds of formula II are known or can be prepared by methods known in the art. For example, the compounds of formula II where a is zero and m is zero are known or can be prepared by reacting the corresponding known siloxane of the formula IV

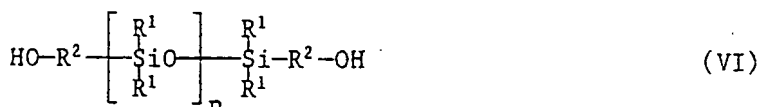


with two equivalents of an alkenyl epoxide of the formula V,

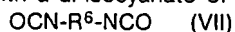


where R<sup>2</sup><sub>0</sub> represents an alkenyl group of 2 to 6 carbon atoms which, upon addition to the siloxane, corresponds to R<sup>2</sup>, to form the corresponding di-epoxide, in the presence of an addition catalyst such as hexachloroplatinic acid at a temperature between about 0°C and 80°C in an inert solvent, and the resulting diepoxide hydrolyzed to the corresponding tetra-ol, of formula II where a is zero and m is zero, by contacting said di-epoxide with methanolic or aqueous base, such as an alkali metal hydroxide, e.g. sodium hydroxide, at a temperature between 0°C and about 80°C.

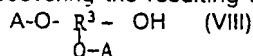
Those compounds of formula I wherein a is one and m is zero can be prepared by end-capping the corresponding known diol of the formula VI



with a di-isocyanate of the formula VII



in a mole ratio of two moles of the compound of formula VII per mole of compound of formula VI in the optional presence of a urethane catalyst, such as dibutyltin-dilaurate or a tri-lower alkyl amine, e.g. triethylamine, or pyridine in the presence or absence of an inert diluent, at a temperature between about 0°C to about 80°C, recovering the resulting diisocyanate, and reacting the diisocyanate with an alcohol of the formula VIII



where R<sup>3</sup> is as defined above and A is hydrogen, such that the corresponding intermediate of formula II where m is zero and a is 1, is produced, in the ratio of two moles of the compound of formula VIII per mole of said diisocyanate optionally in the presence of a urethane catalyst, such as dibutyltin-dilaurate or a tri-lower alkyl amine, e.g. triethylamine, or pyridine, in the presence or absence of a solvent, at a temperature between about 0°C and about 80°C.

Those compounds wherein m is 1, and k is 1, can be prepared from those compounds of formula II where a and m are zero by reacting two moles of the corresponding compound of formula II where m is zero per mole

of isocyanate of formula VII under the conditions recited in the preceding paragraph. Similarly, those compounds where m is 2 and k is 1 can be prepared from those compounds of formula II, wherein a and m are zero by reacting three moles thereof per two moles of diisocyanate of formula VII under the urethane promoting conditions of the preceding paragraph to obtain the corresponding chain extended product of formula II.

Using the same conditions, the diol of formula VI can be chain extended with an di-isocyanate of formula VII in amounts of two moles of diol to three moles of di-isocyanate, or three moles of diol to four moles of di-isocyanate and then the terminal di-isocyanate macromer reacted with the alcohol of formula VIII to obtain the corresponding compound of formula I where m is 1 or 2, k is zero and a is 1.

In the above reactions between isocyanate and alcohol, a solvent may be employed, or the reaction conducted neat. Where a solvent is desirable or necessary, an aprotic solvent, such as methyl ethyl ketone, isopropyl acetate, dimethylsulfoxide or sulfolane may be employed. Also, if the compound of the formula I is to be copolymerized with a liquid monomer, such as methyl methacrylate or dimethylacrylamide, the monomer may advantageously be employed as solvent.

The polysiloxanes of formula I are generally resinous solids, semisolids or viscous liquids varying in number average molecular weight from about 400 to about 100,000, preferably from about 500 to about 10,000 depending on the molecular weight of the polysiloxane employed as starting material and the amount of chain extension.

The polyunsaturated polysiloxanes of formula I can be used by themselves as rapidly ultraviolet or heat-curing compositions or they can be copolymerized with one or more conventional monomers to provide useful polymers. Such polymers can be used as coatings, e.g. by polymerizing the monomer of formula I, alone or with up to 95 percent by weight of conventional comonomers, for the protection of metals, fibers, woods, ceramics or the like, or as biocompatible polymers, including contact lenses, or as gas permeable membranes, especially oxygen permeable membranes. Moreover, the polyfunctional monomers of formula I may be used as polymer cross-linking agents in order to increase the structural integrity of such polymers by providing multiple cross-linking sites. Also, polymers of the polyfunctional monomer are useful upon curing as optical fiber coatings, for example as coatings for poly-methacrylate fibers wherein the fiber is passed through a solution of monomer and cured by placement under an ultraviolet lamp. The resulting coated fiber possesses increased transmissibility of light due to the outer coating of polymer.

Preferred compounds of formula III include 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate. Most preferred is 2-isocyanatoethyl methacrylate. Such compounds and their preparation are disclosed, for example, in US Patent 2,718,516 and British Patent 1,252,099.

Other useful isocyanates of formula III include isocyanato-alkyl vinyl ethers, such as 2-isocyanatobutyl vinyl ether. Also useful are isocyanates obtained by the reaction of one mole of a hydroxy- or amino alkyl acrylate or methacrylate per mole of di-isocyanate of formula VII under the conditions described above for urethane formation. Examples of useful such hydroxy- or amino alkyl acrylates and methacrylates include 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl methacrylate, or t-butylaminoethyl methacrylate and suitable di-isocyanates of formula VII include isophorone diisocyanate, (3,3,4)-trimethylhexane-1,6-diisocyanate, toluene diisocyanate, diphenylmethane-4,4'-diisocyanate and the like.

Yet further preferred compounds of formula III include styrene isocyanate and m-isopropenyl-alpha,alpha-dimethylbenzyl isocyanate.

Diols of formula VI, and the endcapped products thereof with e.g. diisocyanates of formula VII are described for example in US Patents 4,136,250; 4,486,577; and 4,605,712.

A further embodiment of the invention relates to a polymer of the compound of formula I or a copolymer with up to 95 percent by weight of one or more hydrophilic or hydrophobic reactive vinyl monomers, or mixtures thereof, based on the weight of polymer. Preferably the unsaturated polysiloxanes of the present invention are used in combination with other vinyl monomers to make crosslinked polysiloxane-polyvinyl-block copolymers.

The great variety of monomeric reactants make it possible to prepare either hard highly crosslinked copolymers with suitable acrylic, methacrylic or other vinyl monomers, or to prepare soft, rubber like copolymers with low crosslink density.

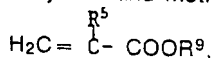
It is also possible to prepare by copolymerization with hydrophilic monomers polysiloxane-hydrogels with water contents ranging up to 80 %.

Reactive monomers which can be employed together with the unsaturated polysiloxanes include mono- or poly-ethylenically unsaturated monomers which undergo polymerization upon exposure to UV-radiation or chemical initiation.

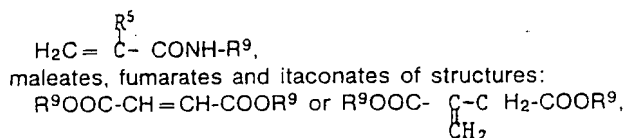
If the polyunsaturated polysiloxanes are to be used in biocompatible materials, especially in either hard or soft contact lenses, a balance of hydrophilic and hydrophobic properties is required and water-soluble as well as water-insoluble comonomers can be used.

The water-insoluble vinyl monomers useful in the present invention are preferably:

Acrylates and methacrylates of the general structure:

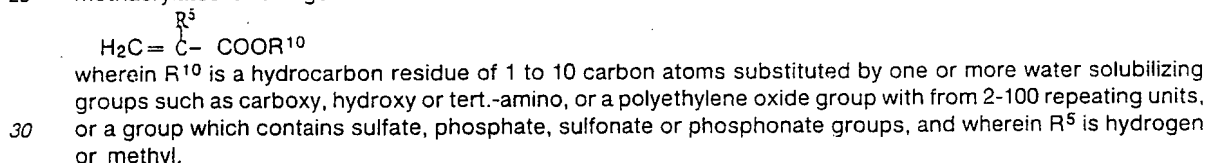


acrylamides and methacrylamides of structure:

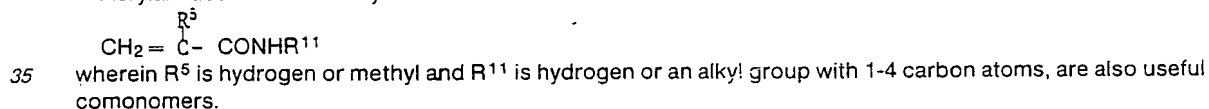


- 5 vinyl esters of structure:  $\text{R}^9-\text{COO}-\text{CH}=\text{CH}_2$   
 and vinyl ethers of structure:  $\text{H}_2\text{C}=\text{CH}-\text{O}-\text{R}^9$   
 wherein  $\text{R}^5$  is hydrogen or methyl and  $\text{R}^9$  is a linear or branched alkyl aliphatic, cycloaliphatic or aromatic group with from 1 to 21 carbon atoms and which may contain ether or thioether linkages or a -CO- group;  $\text{R}^9$  may also be a heterocyclic or a heterocyclic substituted alkyl group containing oxygen, sulfur or nitrogen atoms, or a  
 10 polypropylene oxide or poly-n-butylene oxide group with from 2 to 50 repeating alkoxy units. In addition, the  $\text{R}^9$  group may contain halogen atoms, especially fluorine in form of perfluorinated alkyl groups with from 1-12 carbon atoms; or it may contain dimethylsiloxane groups with from one to six silicon atoms; and may contain -SO- or -SO<sub>2</sub> groups. In case of maleates, fumarates and itaconates one of both  $\text{R}^9$  groups may be hydrogen. Included among the useful monomers are: methyl-; ethyl-; propyl-; isopropyl-; butyl-; isobutyl-; tert.-butyl-; ethoxyethyl-, e.g. 2-ethoxyethyl; methoxyethyl-, e.g. 2-methoxyethyl; benzyl-; 4-t-butylphenyl-; cyclohexyl-; trimethylcyclohexyl-; isobornyl-; dicyclopentadienyl-; norbornylmethyl-; cyclododecyl-; 1,1,3,3-tetramethylbutyl-; n-butyl-; n-octyl-; 2-ethylhexyl-; decyl-; dodecyl-; tridecyl-; octadecyl-; glycidyl; ethylthioethyl-; furfuryl-; 2-butoxyethyl, 2-(2-ethoxyethoxy)ethyl-; hexafluoroisopropyl-; 1,1,2,2-tetrahydroperfluorododecyl-; tri-, tetra- or penta-siloxanyl propyl acrylates and methacrylates, as well as the corresponding amides; N-(1,1-dimethyl-  
 20 3-oxobutyl)acrylamide; mono- and dimethylfumarate, maleate and itaconate; diethyl fumarate; isopropyl and diisopropyl fumarate and itaconate; mono- and diphenyl and methylphenyl fumarate and itaconate; methyl vinyl ether and methoxyethyl vinyl ether; vinyl acetate, vinyl propionate, vinyl benzoate, furthermore, although not covered by the structures hereinbefore, acrylonitrile, styrene, alphanaphthyl styrene and tert-butylstyrene.

Water soluble monomers which are also useful comonomers in the present invention are e.g. acrylates and  
 25 methacrylates of the general structure:



Acrylamides and methacrylamides of structure



Maleates and fumarates of structure  $\text{R}^{10}\text{OOC}-\text{CH}=\text{CH}-\text{COOR}^{10}$  and vinyl ethers of structure  $\text{H}_2\text{C}=\text{CH}-\text{OR}^{10}$  wherein  $\text{R}^{10}$  is as defined above are likewise useful as comonomers as are N-vinyl-lactams, like N-vinyl-2-pyrrolidone.

- 40 Included among the useful water soluble monomers, although not all of them are covered by the structures hereinbefore, are 2-hydroxyethyl-, 2- and 3-hydroxypropyl-, 2,3-dihydroxypropyl-, polyethoxyethyl-, and polyethoxypropylacrylates and methacrylates as well as the corresponding acrylamides and methacrylamides, sucrose-, mannose-, glucose-, sorbitolacrylates and methacrylates; and di-(-2-hydroxyethyl)maleate; acrylamide and methacrylamide, N-methylacrylamide and methacrylamide, bisacetoneacrylamide, 2-hydroxyethylacrylamide, dimethyl-acrylamide and methacrylamide, methylolacrylamide and methacrylamide; vinylformamide and vinylacetamide, N,N-dimethyl- and N,N-diethyl-aminoethyl acrylate and methacrylate as well as the corresponding acrylamides and methacrylamides, N-tert.butylaminoethyl methacrylate and methacrylamide, 2- and 4-vinylpyridine, 4- and 2-methyl-5-vinylpyridine, N-methyl-4-vinyl piperidine, 1-vinyl- and 2-methyl-1-vinylimidazole, para- and orthoaminostyrene, dimethylaminoethyl vinyl ether, N-vinylpyrrolidone,  
 50 and 2-pyrrolidinoethyl methacrylate; acrylic and methacrylic acid, itaconic-, cinnamic-, crotonic-, fumaric-, and maleic acids and lower hydroxyalkyl mono- and diesters thereof, such as 2-hydroxyethyl- and di(2-hydroxyethyl) fumarate, -maleate and -itaconate, and 3-hydroxypropyl-butyl fumarate, and di(polyalkoxy)alkyl-fumarates, maleates and itaconates; maleic-anhydride, sodium acrylate and methacrylate, 2-methacryloyloxyethylsulfonic acid, 2-acrylamido-2-methyl-propanesulfonic acid, 2-phosphatoethyl methacrylate, vinylsulfonic acid, sodium vinylsulfonate, p-styrenesulfonic acid, sodium p-styrenesulfonate, and allyl sulfonic acid.  
 55

Also included are the quaternized derivatives of cationic monomers obtained by quaternization with selected alkylating agents like halogenated hydrocarbons such as methyl iodide, benzyl chloride or hexadecyl chloride; epoxides like glycidol, epichlorohydrin, ethylene oxide; acrylic acid, dimethyl sulfate; methyl sulfate, and propane sultone.

- 60 Preferred monomers for making hard polymers are, in amount of 10-90 % (w/w): methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate or hexafluoroisopropyl methacrylate, styrene, tert.butyl-styrene, or mixtures thereof.

For soft polymers the preferred monomers are: 2-ethylhexyl acrylate, n-butyl acrylate, n-butyl methacrylate,  
 65 n-octyl acrylate, and 2-ethoxyethyl-acrylate, methyl acrylate or mixtures thereof; for hydrogels: 2-hydroxyethyl



methacrylate; N,N-dimethylacrylamide; acrylic and methacrylic acid, N-vinyl-2-pyrrolidone or mixtures thereof.

A wide range of divinyl compounds can be used in addition to the monovinyl compounds. Indeed, from 0 to 50 % by weight of the total monomer can be a diolefinic monomer. Examples of diolefinic monomers are:

Allyl acrylate and methacrylate, ethylene glycol-, diethylene glycol-, triethylene glycol-, tetraethylene glycol-, and generally polyethylene oxide glycol diacrylates and dimethacrylates; 1,4-butane diol and poly-n-butylene oxide glycol diacrylates and dimethacrylates; propylene glycol and polypropylene oxide glycol diacrylates and dimethacrylates; thiodiethylene glycol diacrylate and dimethacrylate; neopentylene glycol diacrylate and dimethacrylate; trimethylolpropane tri and tetraacrylate; pentaerythritol tri and tetraacrylate; divinylbenzene; divinyl ether; divinyl sulfone; disiloxanyl-bis-3-hydroxy propyl diacrylate or methacrylate; bisphenol A diacrylate or dimethacrylate; ethoxylated bisphenol A diacrylate or dimethacrylate; methylene bisacrylamide or methacrylamide, dimethylene bisacrylamide or methacrylamide; N,N'-dihydroxyethylene bisacrylamide or methacrylamide; hexamethylene bisacrylamide or methacrylamide; decamethylene bisacrylamide or methacrylamide; allyl- and diallyl maleate, triallyl melamine, diallyl itaconate, diallyl phthalate, triallyl phosphite, polyallyl sucrose, sucrose diacrylate, glucose dimethacrylate; also, unsaturated polyesters, such as poly-(alkylene-glycol maleates) and poly(alkylene-glycol fumarates), like poly(propylene glycol maleate) and poly(polyalkylene-glycol maleate).

Macromeric divinyl compounds can also be used for copolymerization like polyethylene oxide dimethacrylates, polytetraethylene oxide dimethacrylates (US 4,192,827) or polysiloxane dimethacrylates, (US 4,605,712) or perfluoroether dimethacrylates.

The polyvinyl-polysiloxane of this invention are used either by themselves or together with the mentioned comonomers to make the final oxygen permeable polymers in a last synthesis step by free radical copolymerization, either in bulk or in the presence of small amounts of solvents. The polymerization is suitably carried out with a free radical generating initiator at a temperature in the range from about 40°C to about 105°C, the preferred temperature ranges being between about 50°C and about 100°C. These initiators are preferably peroxides or azo catalysts having half-life at the polymerization temperature of at least 20 minutes. Typical useful peroxy compounds include isopropyl percarbonate, tert.-butyl peroctoate, benzoyl peroxide, lauryl peroxide, decanoyl peroxide, acetyl peroxide, succinic acid peroxide, methyl ethyl ketone peroxide, tert.-butyl peroxyacetate, propionyl peroxide, 2,4-dichlorobenzoyl peroxide, tert.-butyl peroxy-pivalate, pelargonyl peroxide, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, p-chlorobenzoyl peroxide, tert.-butylperoxybutyrate, tert.-butyl peroxy-maleic acid, tert.-butylperoxyisopropyl carbonate, bis(1-hydroxycyclohexyl) peroxide; azo compounds include 2,2-azo-bisisobutyronitrile; 2,2'-azo-bis-(2,4-dimethylvaleronitrile); 1,1'-azo-bis(cyclohexane carbonitrile); and 2,2'-azo-bis(2,4-dimethyl-4-methoxyvaleronitrile).

Other free radical generating mechanisms can be employed, such as x-rays, electron-beams and UV-radiation. Preparation of contact-lens blanks or of fully molded contact lenses by UV radiation in the presence of a photo-initiator such as diethoxyacetophenone, 1-hydroxycyclohexyl phenylketone, 2,2-dimethoxy-2-phenylacetophenone, phenothiazine, diisopropylxanthogendisulfide, benzoin and benzoin derivatives is a preferred method.

The amount of initiator can vary from 0.002 % to 1 % by weight of the monomer and macromer, but is preferably from 0.03 to 0.3 % by weight thereof.

A preferred laboratory method of preparing the polymer, in the form of a cylinder, comprises the filling of flexible polymer tubing with the preferred composition of macromer, monomers, and catalyst and reacting the mixture for approximately 2 hours at 80°C. The finished article is removed by slitting the tubing longitudinally and stripping it away from the polymer article.

Another preferred method for preparing the polymer is by irradiation with ultraviolet light in the presence of a photo-initiator and using plastic molds which are UV transparent, such as molds made of polypropylene or other UV-permeable plastics.

The reaction is preferably carried out in an inert atmosphere if done in open molds. It is known that oxygen inhibits polymerization and gives rise to extended polymerization times. If closed molds are used to form the article, the molds are composed of inert materials having low oxygen permeability and non-stick properties. Examples of suitable molding materials are poly(tetrafluoroethylene), such as Teflon® silicone rubber, polyethylene, polypropylene and polyester, such as MYLAR®. Glass and metallic molds may be used if a suitable mold-releasing agent is employed.

The instant invention also relates to a polymer, suitable for use in contact lenses, comprising the crosslinked copolymerization product of

(A) from about 5 to 100 % by weight of said polymer of a polysiloxane macromer of formula I having a molecular weight from about 400 to about 10,000, said macromer containing at least 3 terminal polymerizable olefinic groups, said groups being attached to the polysiloxane through a urethane linkage, and

(B) 0 to 95 % by weight of said polymer of one or more mono-, di- or trifunctional vinyl monomer polymerizable by free radical polymerization.

More particularly, the instant invention relates to a polymer, suitable for use in contact lenses, comprising the crosslinked copolymerization product of

(A) from about 15 to about 60 % by weight of said polymer of a polysiloxane macromer of formula I having a molecular weight from about 800 to about 10,000, and containing four terminal, polymerizable olefinic groups, and

(B) about 85 to about 40 % by weight of said polymer of water-soluble, or water-insoluble monomers or mixtures thereof, said monomers being monoolefinic, diolefinic or a mixture of monoolefinic and diolefinic monomers.

The polymers of this invention can be tailored so as to be useful either as hard contact lens material or as soft contact lens material. Different comonomers and different levels of polysiloxane macromer are required to get optimal performance in either contact lens type.

In choosing the polysiloxane component and the vinyl monomer for a hard contact lens composition, it is important to arrive at a mixture which will give clear polymers with sufficient dimensional stability and oxygen permeability. Sometimes a mixture of comonomers is advantageous in avoiding phase-separation and thereby opacity. Also, it is easier to obtain clear products with polysiloxanes of relatively low molecular weight than with high molecular weight polysiloxanes. Polysiloxanes with a short chain length between crosslinks also give harder, more dimensionally stable polymers; however, their oxygen permeability is reduced compared to polysiloxanes with longer chain length and therefore lower crosslink density. By a judicious choice of monomer(s) and polysiloxane macromer, one is thus able to tailor to a considerable degree the physical properties and oxygen permeability of the instant silicone polymers from hard and rigid to rubber and soft. In addition to hard and soft contact lenses, because of their good tissue compatibility and oxygen permeability and strength and laticity, the polymers of the present invention are also particularly suitable for use as intramuscular and subcutaneous implants in warm-blooded animals. For the same reasons, the materials of the present invention may be fashioned into substituted blood vessels or extracorporeal shunts.

For preparing hard contact lenses, the preferred polymer comprises the crosslinked copolymerization product of (A) from 15 to 90 % by weight of a polysiloxane macromer of formula I, and (B) from 85 to 10 % by weight of a mixture of water-insoluble monoolefinic monomers, said mixture comprising of 0-15 % water-soluble monoolefinic monomers and 0-20 % diolefinic monomer. The preferred water-insoluble monomers are methyl methacrylate, cyclohexyl methacrylate, tris(trimethylsiloxy)silylpropyl methacrylate, hexafluoroisopropylmethacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, tert-butyl-styrene or mixtures thereof. The preferred water-soluble monomers are 2-hydroxyethyl methacrylate, N,N-dimethylacrylamide, acrylic acid, methacrylic acid, N-vinyl-2-pyrrolidone or mixtures thereof; and the preferred diolefinic monomers are ethylene glycol dimethacrylate and neopentylglycoldiacrylate.

Further preferred is a copolymer comprising the crosslinked copolymerisation product of (A) from 15-85 % of a polysiloxane macromer of formula I wherein a, x and m are zero, A is of the formula Ia, R<sup>4</sup> is of

the formula  $-R^7-\text{O}-\text{C}(=\text{O})-$  wherein R<sup>7</sup> is alkylene of 2 to 6 carbon atoms, R<sup>2</sup> is alkylene of 2 to 4 carbon atoms, each -R<sup>3</sup>(OA)<sub>2</sub> is of the formula AOC<sub>2</sub>H<sub>4</sub>CH(OA)CH<sub>2</sub>- and R<sup>1</sup> is methyl, and a) 15-85 % of a first comonomer selected from methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, hexafluoroisopropyl methacrylate, t-butyl methacrylate, styrene, and t-butyl styrene; b) 0-15 % of a second comonomer selected from acrylic acid, methacrylic acid, and maleic anhydride; and c) 0-20 % of ethylene glycol dimethacrylate or neopentylglycol diacrylate.

Even preferred is a copolymer comprising the crosslinked copolymerisation product of (A) from 15-85 % of a polysiloxane macromer of formula I wherein A is of the formula Ib, a is one, m is zero, R<sup>3</sup>(OA)<sub>2</sub> is of the formula (AOC<sub>2</sub>H<sub>4</sub>)<sub>2</sub>CH-, R<sup>5</sup> is methyl and R<sup>1</sup> is methyl, and a) 15-85 % of a first comonomer selected from methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, hexafluoroisopropyl methacrylate, t-butyl methacrylate, styrene, and t-butyl styrene; b) 0-15 % of a second comonomer selected from acrylic acid, methacrylic acid, and maleic anhydride; and c) 0-20 % of ethylene glycol dimethacrylate or neopentylglycol diacrylate.

Also preferred is a copolymer comprising the crosslinked copolymerisation product of (A) from 15-60 % of a polysiloxane macromer of formula I wherein m is 1 or 2, k is one, a is zero, A is of the formula Ia, x is zero, -R<sup>3</sup>(OA)<sub>2</sub> is of the formula AOC<sub>2</sub>H<sub>4</sub>CH(OA)CH<sub>2</sub>-, R<sup>5</sup> is methyl and R<sup>1</sup> is methyl or wherein m is 1 or 2, k is one, a is zero, A is of the formula Ia, x is zero, -R<sup>3</sup>(OA)<sub>2</sub> is of the formula AOC<sub>2</sub>H<sub>4</sub>CH(OA)CH<sub>2</sub>-, R<sup>5</sup> is methyl, R<sup>1</sup> is methyl and wherein R<sup>2</sup> is ethylene and R<sup>6</sup> is a divalent hydrocarbyl aliphatic, cycloaliphatic, aromatic or araliphatic group of up to 16 carbon atoms, and a) 40-85 % of a first comonomer selected from methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, hexafluoroisopropyl methacrylate, t-butyl methacrylate, styrene, and t-butyl styrene; b) 0-15 % of a second comonomer selected from acrylic acid, methacrylic acid, and maleic anhydride; and c) 0-20 % of ethylene glycol dimethacrylate or neopentylglycol diacrylate.

Although this invention is primarily directed toward the synthesis of hard contact lens materials, it is also possible to make soft contact lens materials as well as hydrogel type contact lenses.

For preparing contact lenses with low water absorption, the preferred polymer comprises the crosslinked copolymerization product of (A) 30 to 80 % by weight of a polysiloxane macromer of formula I and (B) 70 to 20 % by weight of water-insoluble monoolefinic monomer, or monomer mixture containing up to 10 % water soluble monoolefinic monomer.

For making soft contact lenses the preferred water-insoluble monomers are methyl acrylate, ethyl acrylate or methacrylate, n-butyl acrylate or methacrylate, n-hexyl acrylate or methacrylate, 2-ethylhexyl acrylate or methacrylate, n-octyl acrylate or methacrylate, n-decyl acrylate or methacrylate and oligo-siloxanyl alkyl methacrylates, like tris-(trimethyl siloxanyl)silyl-propyl-methacrylate.

For preparing hydrogel contact lenses, the preferred polymer comprises the crosslinked copolymerization

product of 20 to 60 % by weight of a polysiloxane macromer of formula I, with from 80 to 40 % by weight of primarily water-soluble monomers. The preferred water-soluble monomers are N,N-dimethylacrylamide, N-vinyl-2-pyrrolidone, 2-hydroxyethyl methacrylate, acrylamide, or mixtures thereof.

The polysiloxane-copolymers of this invention may also be treated by any of the commonly used methods used to increase the wettability of hydrophobic surfaces, such as plasma-treatment and irradiation-grafting and oxidation.

The contact lenses made from the polymers of this invention are fillerless, hydrolytically stable, biologically inert, transparent and sufficiently permeable to oxygen to allow the transport of oxygen generally sufficient to meet the requirements of the human cornea.

The following examples are presented for the purpose of illustration only and are not to be construed to limit the nature and scope of the instant invention in any manner whatsoever.

In the following examples, specific oxygen permeability ( $O_2$ -DK) is determined by measuring oxygen permeability at indicated temperatures and thickness with a CREATECH PERMEOMETER, using a polarographic electrode in an air-saturated aqueous environment and is expressed in units of DK where DK is  $\text{cm}^2/\text{sec} (\text{mlO}_2/\text{ml mmHg}) \times 10^{11}$ .

As reference materials for  $O_2$ -DK measurements, water swollen poly(2-hydroxyethyl methacrylate) (poly-hema; 39 % water content; a common soft-lens material) and CAB, cellulose-acetate-butyrate (an oxygen-permeable hard-lens material) are used; for hardness CAB and poly(methyl methacrylate) are used as reference materials. The  $O_2$ -DK, Shore-D and contact angle values for these materials are given below.

Hardness is determined using a Shore-D durometer on polished surfaces of center cut buttons of 10 mm diameter and 8 mm height.

Reference Material	$O_2$ -DK	Shore-D
poly-hema (39 % $\text{H}_2\text{O}$ )	7.5	-
poly(methyl methacrylate)	<0.1	92
cellulose-acetate-butyrate	8.2	80

#### Example 1:

26.7 g (0.0872 equivalents of hydroxy groups) of a polysiloxane-dialkyltetrol (MW 1226) of the structure of formula II where m and a are zero,  $\text{R}^1$  is methyl,  $\text{R}^2$  is  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ , each  $-\text{R}^3(\text{OH})_2$  is  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2-$ , and n is about 12, are mixed in a reaction flask with 13.5 g (0.0871 mol) isocyanatoethyl methacrylate (IEM, from DOW Chem. Corp.) and 0.02 g dibutyltindilaurate (DBTL). The mixture is stirred under a dry nitrogen blanket at  $50^\circ\text{C}$  until all NCO groups have disappeared, as determined by IR spectroscopy. The slightly more viscous reaction product, consisting of a polysiloxane terminated on both ends with bis-methacrylatealkyl groups, is stored in the dark under nitrogen.

#### Example 2:

64.50 g (0.064 eqv) of a polysiloxane-dialkyltetrol (MW 4031), identical to that of example 1, except that n is approximately 52 are mixed in a reaction flask with 13.28 g (0.064 eqv) m-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate (m-TMI), from Am. Cyan. Co.) and 0.028 g DBTL. The mixture is stirred under dry nitrogen at  $24^\circ\text{C}$  until all NCO groups have disappeared, as determined by IR. The clear, viscous reaction product, consisting of a polysiloxane terminated at both ends with urethane connected  $\alpha$ -methyl styryl groups is stored in the dark under nitrogen.

#### Example 3 and 4:

Using the same procedure as described in example 1, polysiloxane tetramethacrylates are prepared by reacting the reactants listed in the table, wherein the polysiloxane dialkyltetrols are identical to example 1 except for the value of n:

Example	n	Polysiloxane-Tetrol			IEM	
		MW	g	eqv.	g	mol
3	40	3404	19.4	0.0228	3.53	0.0227
4	77	6287	19.0	0.0121	1.07	0.0120

Examples 5-9:

Synthesis of polymers useful as oxygen permeable hard contact lenses:

50 g of the PDMS (=polydimethylsiloxane)-tetramethacrylate of example 1 are dissolved in 50 g freshly distilled methyl methacrylate (MMA) together with 0.02 g benzoin methyl ether (BME). The mixtures are three times degassed in vacuo and under a nitrogen blanket, filled into round polypropylene button molds of 1 cm height and 1 cm diameter. The molds are exposed to UV light for 5 hours, then heated to 100°C and allowed to slowly cool to room-temperature. 0.2 mm thick slices are cut and polished and their oxygen permeability is determined to be 20 (barrers), with a Shore-D hardness of 74.

Using the same procedure the following polymers are prepared and their hardness and oxygen permeability measured:

Ex. No.	Composition %				Shore-D	O <sub>2</sub> -DK (barrers) 0.25 mm/22°C
	Tetra-MA of ex.	%	MMA	TMMA 1)		
5	1	50	-	50	73	28
6	3	40	60	-	79	36
7	4	40	60	-	73	78
8	3	40	-	60	75	44
9	2+3 (1:1)	40	60	-	77	52

1) TMMA = trimethyl-cyclohexyl methacrylate

Examples 10-21:

Using the procedure of example 5 the following polymers are prepared and their physical properties determined. All samples contain 9 % methacrylic acid.

Ex. No.	Composition				Shore-D hardness	O <sub>2</sub> -DK (barrers) at 0.25 mm and 22°C
	Tetra MA of ex.	MA %	Comonomer 1) type	%		
10	3	40	MMA	51	79	35
11	3	40	TMMA	51	77	41
12	3	40	IBMA	51	79	33
13	3	40	CYMA	51	78	29
14	3	38	MMA	53	80	32
15	3	38	TMMA	53	78	35
16	3	38	IBMA	53	80	29
17	3	35	MMA	56	81	22
18	3	35	TMMA	56	80	23
19	4	40	CYMA	51	72	55
20	4	40	MMA	51	70	61
21	4	40	TMMA	51	71	53

1) MMA methyl-methacrylate

TMMA trimethyl cylcohexyl-methacrylate

IBMA isobornyl-methacrylate

CYMA cyclohexyl-methacrylate

#### Examples 22-24:

Using the same procedure as described in example 5 the following polymers are prepared and their physical properties determined. All samples contain 9 % methacrylic acid.

Ex. No.	Composition (%)		Shore-D hardness	O <sub>2</sub> -DK (barrers) at 0.25 mm and 22°C
	Tetra MA of ex. 1(%)	MMA %		
22	55	36	86	7.5
23	75	16	82	19
24	85	6	78	37.0

#### Example 25:

The tetra-styryl PDMS macromer of example 2 is used to make a polymer according to the procedure described in example 5 with the following composition and properties:  
38 % PDMS-tetra-styryl of example 2;

53 % MMA,  
9 % methacrylic acid  
Shore-D hardness: 82; O<sub>2</sub>-DK (barrers): 25 (0.25 mm/22°C).

5 Examples 26 and 27:

Following the procedure of example 5 the following two polymers are synthesized and evaluated:

Composition	Ex. 26	Ex. 27
PDMS-tetramethacrylate of Ex. 3	35 %	30 %
MMA	48 %	53 %
hexafluoroisopropyl-methacrylate (HFMA)	8 %	8 %
methacrylic acid (MAA)	9 %	9 %
Shore-D hardness	81	84
O <sub>2</sub> -DK (barrers) (0.25 mm/22°C)	32	20

25 Examples 28-30:

The polymers of examples 10, 20 and 17 are prepared in form of 1 mm thick sheets by casting them in a MYLAR® lined glass mold, using a 1 mm silicone-cord spacer and held together by clamps. The sheets are tested for physical properties on an INSTRON testing apparatus.

Ex. No.	Pol. of Ex.	MW of tetrol	Tensile Str. (kg/mm <sup>2</sup> )	Youngs Mod.	Elongation (%)
28	10	3404	3.62	85.2	17.3
29	20	6287	3.11	68.6	21.7
30	17	3404	3.73	80.1	8.6

45 Example 31:

Synthesis of chain extended PDMS-polyacrylates.

50 Step I:

64.50 g (0.016 m) of the polydimethylsiloxane tetrol (PDMS) of example 2 having a MW of 4031 are mixed in a reaction flask with 1.78 g (0.009 m) isophorone diisocyanate (IPDI) and 0.027 g DBTL. The mixture is stirred under a dry-N<sub>2</sub> blanket for 12 hours at 25°C until all NCO groups have disappeared. The viscous reaction product has an equ. weight of 1388.5 (theo.: 1380.7) (MW calc: 8330.7).

55 Step II:

5.0 g (0.0006 mole) of the chain extended hex-ol (MW 8330.7) are dissolved in 5.37 g of methyl methacrylate and then 0.37 g (0.0024 mole) of isocyanatoethyl methacrylate are added. The mixture is mixed under a dry N<sub>2</sub> blanket for 16 hours at 25°C until all -NCO functionality has disappeared as determined by IR analysis.

60 Examples 32-34:

Using the same step I procedure, chain extended polyols are prepared, but using a tetrol of 1219 MW and instead of a 2:1 (tetrol:IPDI) mol-ratio a mol ratio of 3:2, giving a chain extended polyol of equ. w. 530.5 (MW calc. = 4244), which theoretically is a octa-hydroxy compound.

65 Both chain-extended polyols are reacted as described for step II above with IEM in the following mol ratios:

Ex.	PDMS-tetrol/diisocyanate (MW)	mol-ratio	OH-functionality of product	Moles IEM added
31	4031	2:1	6	4
32	4031	2:1	6	3
33	4031	2:1	6	5.9
34	1219	3:2	8	4

Examples 35-38:

Synthesis of hard contact lens buttons.

2.45 g of the chain extended PDMS tetramethacrylate mixtures (50 % in methyl methacrylate) are mixed with 0.73 g of methyl methacrylate and 0.32 g of methacrylic acid and 0.007 g of benzoin methyl ether. The mixture, consisting of 35 % PDMS-acrylate, 56 % MMA and 9 % MAA, is degassed, then filled into contact lens button molds and polymerized by UV light for 4 hours, then heated at 100°C for 1 hour. Hard clear buttons are obtained. The Shore-D hardness is determined to be 75.

Using the same procedure, clear buttons with the same compositions are prepared from the PDMS-methacrylates of examples 32-34.

Ex.	PDMS-methacrylate of Ex.	Shore-D
35	31	75
36	32	73
37	33	77
38	34	84

The polymer of ex. 38 has an oxygen permeability DK of 31.5 (barrers) (0.27 mm/24°C).

Example 39:

Synthesis of PDMS-tetramethacrylate from a PDMS-di-alkanol, diisocyanate and glycerol-dimethacrylate.

24.0 g (0.01 m) of a polydimethylsiloxane-dipropanol of MW 2400 (Shin-Etsu X-61-A1000) are placed into a reaction flask equipped with stirrer, condenser and N<sub>2</sub>-sparge, 4.67 g (0.021 m) isophorone diisocyanate are added together with 0.01 g dibutyltin-dilaurate. The mixture is stirred at 24°C for 24 hours, until the NCO-content has fallen to 1/2 of its original value, as determined by titration. 29.75 g methyl methacrylate (MMA) are added to 25.7 g of this NCO-prepolymer to reduce the viscosity, followed by 4.09 g (0.0208 m) glycerol-dimethacrylate (Rohm Tech.). The mixture is stirred at 24°C until all NCO has disappeared.

The PDMS-tetra-methacrylate is further diluted with MMA and methacrylic acid (MAA) to give a composition of 35 % tetra-methacrylate, 56 % MMA and 9 % MAA. Contact lens buttons are prepared as described in examples 5-9; the polymer is clear and hard, with a Shore-D hardness of 82 and an oxygen-permeability DK of 13 (barrers) at 22°C/0.2 mm thickness.

Example 40:

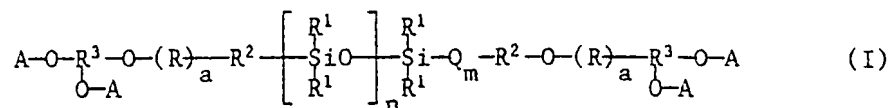
The bis-tetramethacrylate monomer product of example 1 is placed into a beaker and a length of polymethacrylate fiber, having a diameter of 25 mm and a smooth surface, placed therein. The fiber is drawn vertically from the beaker with a thin film of monomer adhering to the surface of the fiber. The monomer is polymerized by subjecting the treated fiber to an ultraviolet light source. The resulting fiber with the crosslinked polymer coating is suitable for use as an optical waveguide.

## Claims

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1. A poly-unsaturated polysiloxane of the formula I,

10



15

wherein a is zero or one;

n is 2 to about 500;

m is zero to 2;

20

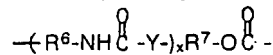
at least three of A either consist of a reactive vinyl containing group of the formula Ia or Ib, and the remaining A are hydrogen or said reactive vinyl containing group:

25



where R<sup>4</sup> is arylene of 6 to 12 carbon atoms, alkarylene of 7 to 14 carbon atoms, alkylene of up to 8 carbon atoms, alkyleneoxy of up to 8 carbon atoms or a group of the formula

30



where R<sup>7</sup> is alkylene of 2 to 8 carbon atoms, x is zero or one, Y is -O- or -NR<sup>8</sup>- where R<sup>8</sup> is hydrogen or alkyl of up to 4 carbon atoms, and R<sup>6</sup> is the diradical residue of an aliphatic, cycloaliphatic, aromatic or araliphatic diisocyanate;

35

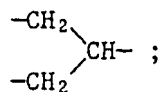
R<sup>5</sup> is hydrogen or methyl;

R<sup>1</sup> is alkyl of up to 4 carbon atoms or phenyl;

R<sup>2</sup> is alkylene of 2 to 6 carbon atoms;

R<sup>3</sup> is -CH<sub>2</sub>-CH-CH<sub>2</sub>- or

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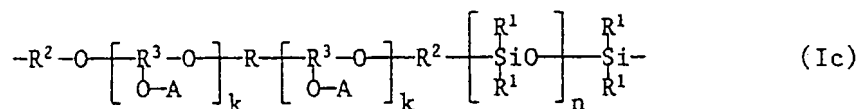


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such that -R<sup>3</sup>(OA)<sub>2</sub> is AOCH<sub>2</sub>CH(OA)CH<sub>2</sub>- or (AOCH<sub>2</sub>)<sub>2</sub>CH-;

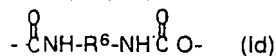
Q is a group of the formula Ic,

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where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, A and n are as defined above; and k is zero or one; and R is a group of the formula Id



where R<sup>6</sup> is as defined above.

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2. A polysiloxane according to claim 1, wherein R<sup>1</sup> is methyl.

3. A polysiloxane according to claim 1, wherein a, x and m are zero, A is of the formula Ia, R<sup>4</sup> is of the formula

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-R<sup>7</sup>-O-C(=O)- wherein R<sup>7</sup> is alkylene of 2 to 6 carbon atoms, R<sup>2</sup> is alkylene of 2 to 4 carbon atoms and each -R<sup>3</sup>(OA)<sub>2</sub> is of the formula AOCH<sub>2</sub>CH(OA)CH<sub>2</sub>-.



4. A polysiloxane according to claim 3, wherein  $R^2$  is ethylene, each A is of the formula Ia and  $R^5$  is methyl.
5. A polysiloxane according to claim 3, wherein  $R^1$  is methyl.
6. A polysiloxane according to claim 1, wherein A is of the formula Ib, a is one, m is zero,  $R^3(OA)_2$  is of the formula  $(AOCH_2)_2CH-$  and  $R^5$  is methyl. 5
7. A polysiloxane according to claim 1, wherein m is 1 or 2, k is one, a is zero, A is of the formula Ia, x is zero,  $-R^3(OA)_2$  is of the formula  $AOCH_2CH(OA)CH_2-$  and  $R^5$  is methyl.
8. A polysiloxane according to claim 7, wherein  $R^2$  is ethylene and  $R^6$  is a divalent hydrocarbyl aliphatic, cycloaliphatic, aromatic or araliphatic group of up to 16 carbon atoms.
9. A polysiloxane according to claim 1, wherein A is of the formula Ib, a is one, m is 1 or 2, k is zero,  $-R^3(OA)_2$  is of the formula  $(AOCH_2)_2CH-$  and  $R^5$  is methyl. 10
10. A polysiloxane according to claim 9, wherein  $R^2$  is ethylene and  $R^6$  is a divalent hydrocarbyl aliphatic, cycloaliphatic, aromatic or araliphatic group of up to 16 carbon atoms.
11. A polymer of the compound of formula I according to claim 1, alone, or as a copolymer with up to 95 percent by weight of one or more hydrophilic or hydrophobic reactive vinyl monomers, or mixtures thereof, based on the weight of polymer. 15
12. A copolymer according to claim 11 comprising the crosslinked copolymerization product of
  - (A) from about 5 to 100 % by weight of said polymer of a polysiloxane macromer of formula I having a molecular weight from about 400 to about 10,000, said macromer containing at least 3 terminal polymerizable olefinic groups, said groups being attached to the polysiloxane through a urethane linkage, and
  - (B) 0 to 95 % by weight of said polymer of one or more mono-, di- or trifunctional vinyl monomer polymerizable by free radical polymerization. 20
13. A copolymer according to claim 11, with from about 15 to about 60 percent by weight of the macromer of formula I and about 85 to about 40 percent by weight of reactive monoolefinic or diolefinic, water-soluble or water-insoluble monomer, or mixture thereof. 25
14. A copolymer according to claim 11, comprising the crosslinked copolymerization product of
  - (A) from about 15 to about 60 % by weight of said polymer of a polysiloxane macromer of formula I having a molecular weight from about 800 to about 10,000, and containing four terminal, polymerizable olefinic groups, and
  - (B) about 85 to about 40 % by weight of said polymer of water-soluble, or water-insoluble monomers or mixtures thereof, said monomers being monoolefinic, diolefinic or a mixture of monoolefinic and diolefinic monomers. 30
15. A copolymer according to claim 11, with from 15 to 90 percent by weight of the macromer of formula I and 85 to 10 percent of a mixture of reactive water-insoluble monoolefinic monomers, said mixture comprising 0-15 % water-soluble monoolefinic monomers and 0-20 % diolefinic monomer. 35
16. A copolymer according to claim 11, with from 30 to 80 percent by weight of the macromer of formula I and 70 to 20 percent by weight of a water-insoluble monoolefinic monomer, or monomer mixture containing up to 10 % water soluble monoolefinic monomer.
17. A copolymer according to claim 11, with from 20 to 60 percent by weight of the macromer of formula I and 80 to 40 % by weight of primarily water-soluble monomers. 40
18. A copolymer according to claim 11 comprising the crosslinked copolymerisation product of
  - A) 15-85 % of the polysiloxane of claim 5;
  - a) 15-85 % of a first comonomer selected from methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, hexafluoroisopropyl methacrylate; t-butyl methacrylate, styrene, and t-butyl styrene;
  - b) 0-15 % of a second comonomer selected from acrylic acid, methacrylic acid, and maleic anhydride; and
  - c) 0-20 % of ethylene glycol dimethacrylate or neopentylglycol diacrylate. 45
19. A copolymer according to claim 11 comprising the crosslinked copolymerisation product of
  - A) 15-85 % of the polysiloxane of claim 6 wherein  $R^1$  is methyl;
  - a) 15-85 % of a first comonomer selected from methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, hexafluoroisopropyl methacrylate, t-butyl methacrylate, styrene, and t-butyl styrene;
  - b) 0-15 % of a second comonomer selected from acrylic acid, methacrylic acid, and maleic anhydride; and
  - c) 0-20 % of ethylene glycol dimethacrylate or neopentylglycol diacrylate. 50
20. A copolymer according to claim 11 comprising the crosslinked copolymerisation product of
  - A) 15-60 % of the polysiloxane of claim 7 or 8 wherein  $R^1$  is methyl;
  - a) 40-85 % of a first comonomer selected from methyl methacrylate, cyclohexyl methacrylate, trimethylcyclohexyl methacrylate, isobornyl methacrylate, hexafluoroisopropyl methacrylate, t-butyl methacrylate, styrene, and t-butyl styrene;
  - b) 0-15 % of a second comonomer selected from acrylic acid, methacrylic acid, and maleic anhydride; and
  - c) 0-20 % of ethylene glycol dimethacrylate or neopentylglycol diacrylate. 55

- 21. A contact lens formed of a polymer or copolymer according to claim 11.
- 22. A contact lens formed of a copolymer according to claim 13.
- 23. A contact lens formed of a copolymer according to any of claims 15, 16 or 17.
- 24. A contact lens formed of a copolymer according to any of claims 18, 19 or 20.

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